

Supplementary Materials

A brief introduction of the background and experimental details of the unpublished data in this paper.

1.1 Materials and Methods in the ferrihydrite aging studies

It was reported that boiling for hours in strong alkaline solution would favor the transformation of ferrihydrite to its crystalline counterparts (Schwertmann, 1966), and organic carbon could have an inhibitory effect on this process. This experiment was conducted to examine that to what extent the DOM from different fertilization treated soils could inhibit the aging of ferrihydrite.

Surface soils (0-20 cm) were collected from the Qiyang long-term fertilization station (Wen et al., 2014). Soils under the following three fertilization treatments were collected from the long-term experimental site in 2015: (1) without fertilization (Control), (2) chemical fertilization as nitrogen, phosphorus and potassium fertilizers (NPK), and (3) a combination of chemical fertilization and organic amendments (NPKM). Soil DOM from the three treatments were extracted as previously described (Wen et al., 2014). Ferrihydrite was synthesized as previously described (Schwertmann and Cornell, 2008).

5 g of the synthetic ferrihydrite was added in 50 mL 1 M KOH solution, with DOM extracted from different fertilized soils, and aging for 4 hours at 100 °C. Seven treatments were set as: (1) Ferrihydrite, (2) Ferrihydrite + Control, (3) Ferrihydrite + NPK, (4) Ferrihydrite + NPKM, (5) Ferrihydrite + NPKM/5, (6) Ferrihydrite + H₂O₂ + NPKM, and (7) NPKM + H₂O₂. Note that 15% H₂O₂ was used to destroy the organic carbon in the reaction system, and NPKM/5 represented that the DOM from the NPKM-treated soil was diluted by 5 times so that the DOC concentration was compatible to that in the NPK-treated soil.

After aging, all samples were air-dried, ground, and brushed onto tapes, which were stacked together for the Fe K-edge XANES analyses. The detailed description for the Fe XANES could be found elsewhere (Wen et al., 2018).

1.2 Materials and Methods in the adsorption and co-precipitation experiments

Soil sampling and soil DOM extracting procedures were the same as the ferrihydrite aging experiment and not repeated here.

For the co-precipitation assays: 0.2 g Fe(NO₃)₃·9H₂O was mixed with 200 mL of a DOM solution extracted from different fertilized soils under vigorous stirring (650 rpm). The pH of the suspensions was raised to 7 by slowly adding 0.1 M NaOH.

For the adsorption assays: 50 mg of the synthetic ferrihydrite were added to 200 mL of the DOM solution extracted from different fertilized soils, producing the same molar C/Fe ratios as in the co-precipitation assays. The suspensions were adjusted to pH values of 4 and 7 by adding NaOH or HCl. After 24 h of shaking adsorption and coprecipitation suspensions at 60 rpm in the dark, the suspensions were centrifuged at 20 000 g for 30 min. The settled material was washed twice and then freeze dried for the Fe K-edge XANES analyses. The detailed description for the Fe XANES could be found elsewhere (Wen et al., 2018).

Table S1 The correlation (r) and significance values (P) of linear regressions between Fe fractions, SOC and C functional groups in soil colloids from Qiyang long-term fertilization site. Statistical analyses of data (means \pm SD, $n = 3$) were performed in the R Studio (Version: 0.99.903). The Pearson's correlation coefficient (r) was used to evaluate the linear correlation between reactive Fe minerals and C functional groups.

	SOC		Aromatic C		C-C(H)		C-O		C=O		C(O)O	
	P	r	P	r	P	r	P	r	P	r	P	r
Ferrihydrite	< 0.01	0.78 **	< 0.01	0.96 **	0.1	0.01	0.3	-0.58	< 0.01	0.97 **	0.5	0.43
Goethite	0.2	-0.72	< 0.05	-0.91 *	0.9	-0.04	0.3	0.59	< 0.05	-0.90 *	0.4	-0.48
Fe _t	0.3	-0.59	< 0.01	-0.98 **	0.7	-0.26	0.1	0.77	< 0.05	-0.90 *	0.2	-0.64
Fe _{co}	0.2	0.66	0.2	0.67	0.8	-0.18	0.7	-0.26	0.1	0.78	0.9	-0.03
Fe _d	0.6	-0.31	< 0.05	-0.94 *	0.3	-0.55	< 0.05	0.94 *	0.1	-0.75	0.1	-0.83
Fe _o	0.1	0.80	0.05	0.87	0.8	-0.13	0.5	-0.43	< 0.05	0.96 *	0.8	0.17
Fe _p	0.3	-0.60	< 0.01	-0.96 **	0.7	-0.23	0.2	0.74	< 0.05	-0.88 *	0.3	-0.63
Fe _{o-p}	< 0.05	0.76 *	< 0.01	0.96 **	0.9	0.01	0.3	-0.58	< 0.01	0.98 **	0.5	0.36

Note: * represent $0.01 < P < 0.05$, **represent $0.001 < P < 0.01$, ***represent $P < 0.001$ 。

The data for ferrihydrite and Goethite is from the LCF results of Fe K edge XANES (Wen et al., 2019); Different Fe fractions (Fe_t, Fe_{co}, Fe_d, Fe_o, Fe_p, Fe_{o-p}) data are from the chemical extraction methods (Table 1); The data for SOC is from CN analyzer (Table 1); and the C fractions are from the XPS fitting results (Table S3).

Table S2 The correlation (r) and significance (P) values of linear regressions between Fe fractions and C functional groups in soil colloids from Qiang, Gongzhuling, Shenyang and Urumqi sites (Wen et al., 2019).

	SOC		Aromatic C		C-C(H)		C-O		C=O		C(O)O	
	P	r	P	r	P	r	P	r	P	r	P	r
Fe _o	0.05	-0.57	0.29	-0.33	0.60	0.17	0.92	-0.03	0.11	0.49	0.74	-0.11
Fe _p	0.05	-0.58	0.33	-0.31	0.34	0.03	0.85	-0.06	0.43	0.25	0.41	-0.26
Fe _d	0.19	-0.40	0.55	-0.19	0.72	0.12	0.78	0.09	0.84	-0.07	0.70	-0.12
Fe _{o-p}	0.96	0.02	0.88	-0.05	0.44	-0.25	0.87	0.05	0.13	0.47	0.34	0.30
Ferrihydrite	<0.01	0.71	<0.01	0.72	0.06	-0.56	0.96	-0.02	0.42	0.26	0.99	0
Goethite	0.07	-0.54	0.32	-0.32	0.40	0.27	0.98	-0.01	0.97	0.01	0.71	-0.12
Lepidocrocite	0.60	0.17	0.97	0.01	0.80	0.08	0.86	0.06	0.22	-0.38	0.71	-0.12

Table S3 Dissolved organic carbon (DOC) concentration (measured by TOC/TN analyzer (multi N/C 3000, Analytik Jena AG, Germany)) and X-ray photoelectron spectroscopy-based speciation of carbon binding environments in water-dispersible soil colloids under a long-term fertilization regimen (in atom%) from Qiyang site (Wen et al., 2019).

Fertilization regimen	DOC concentration (mg L ⁻¹)	Chemical species				
		Ar-C-C(H)	C-C(H)	C-O	C=O	C(O)O
		284.2 eV	284.8 eV	286.2 eV	287.9 eV	289 eV
Control	22.19 (0.85)	17.12	60.41	13.20	3.70	5.57
NPK	41.17 (0.14)	10.18	40.78	44.65	3.05	1.34
NPKM	212.5 (1.52)	20.78	47.64	22.42	5.89	3.27

Supplementary References:

- Schwertmann, U. (1966). Inhibitory effect of soil organic matter on the crystallization of amorphous ferric hydroxide. *Nature* 212(5062), 645-646. doi: <https://doi.org/10.1038/212645b0>.
- Schwertmann, U., and Cornell, R.M. (2008). *Iron oxides in the laboratory: preparation and characterization*. John Wiley & Sons.
- Wen, Y., Li, H., Xiao, J., Wang, C., Shen, Q., Ran, W., et al. (2014). Insights into complexation of dissolved organic matter and Al(III) and nanominerals formation in soils under contrasting fertilizations using two-dimensional correlation spectroscopy and high resolution-transmission electron microscopy techniques. *Chemosphere* 111, 441-449. doi: [10.1016/j.chemosphere.2014.03.078](https://doi.org/10.1016/j.chemosphere.2014.03.078).
- Wen, Y., Xiao, J., Liu, F., Goodman, B.A., Li, W., Jia, Z., et al. (2018). Contrasting effects of inorganic and organic fertilisation regimes on shifts in Fe redox bacterial communities in red soils. *Soil Biol. Biochem.* 117, 56-67. doi: <https://doi.org/10.1016/j.soilbio.2017.11.003>.
- Wen, Y.L., Liu, W.J., Deng, W.B., He, X.H., and Yu, G.H. (2019). Impact of agricultural fertilization practices on organo-mineral associations in four long-term field experiments: Implications for soil C sequestration. *Sci. Total Environ.* 651, 591-600. doi: [10.1016/j.scitotenv.2018.09.233](https://doi.org/10.1016/j.scitotenv.2018.09.233).